THE RELATION OF MESOMERIC EFFECTS AND ULTRAVIOLET LIGHT ABSORPTION DATA

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A THESIS

by

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ABSTRACT

A method for the determination of mesomeric effects from ultraviolet light absorption data is critically discussed. For halogen-substituted compounds, the method gives an order of mesomeric effects different from that which is usually accepted for the halogens.

THE RELATION OF MESOMERIC EFFECTS AND ULTRAVIOLET LIGHT ABSORPTION SPECTRA

INTRODUCTION

It has been shown that the spectra of para-substituted benzoic acids may be related to the mesomeric, but not to the inductive effect of the substituent group.[16] It was shown in particular that both wave-length displacements towards longer wave-lengths, and intensities of absorption (ε) for the halogen-substituted compounds were in the order -I > -Br > -Cl > -F.

Electronic spectra, like other physical properties, require consideration primarily of the ground states of molecules; these will determine the excited states, and the main difference between the ground and excited states will be that the proportion of contributing forms will vary. Thus the electron-displacement effects which we chiefly have to take into account will be the inductive and mesomeric effects. Although the halogen substituent also introduces additional "polarisability" into the structure, which may well alter, for example, the rates of reaction of various halogen-substituted

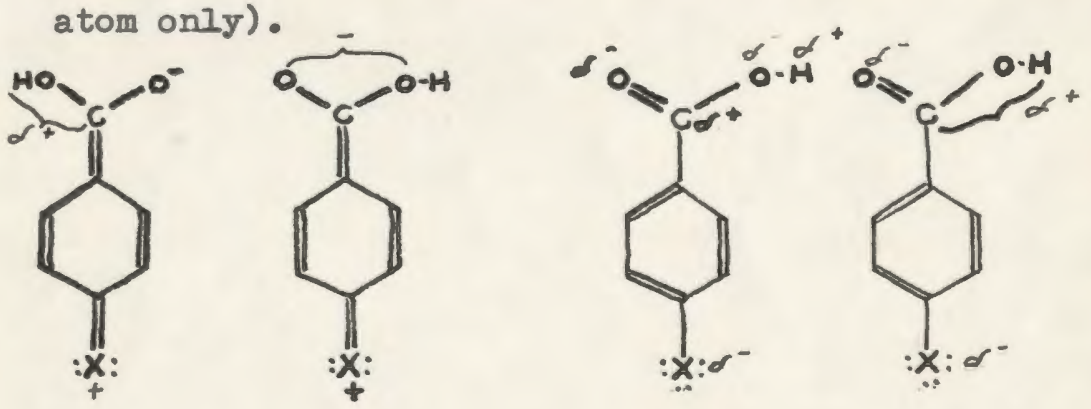
compounds, electronic spectra of the type discussed would be expected to be proportional to "polarisation" effects. Further, a shift to longer wave-length accompanied by increased intensity of absorption, represents a "closing-up" of electronic levels of the ground and excited states and thus a decrease in transition energy. Since the excited states have been shown to be mainly dipolar, these dipolar forms will contribute more to the excited than to the ground states.[21] This "closing-up" of the energy levels therefore represents a more ready formation of excited states. Hence, the data show that the dipolar states are attained more easily in the order -I > -Br > -Cl > -F, that is, the potential energy of the excited states is lowered in the order -I > -Br > -Cl > -F. Since it is conclusively established that inductive effects are in the order -F > -Cl > -Br > -I,[20,23] which would indicate the reverse order of the observed effects, one is lead to the conclusion that probably the mesomeric effect may account for the observed data. This supposes the mesomeric effect to be in the order -I > -Br > -Cl > -F, again the reverse of the accepted order, but the evidence for the mesomeric effect being in the order -F > -Cl > -Br > -I appears to be far less conclusive than the evidence for the inductive effects.[23]

Another possible interpretation is that the spectral effects are determined chiefly by "polarisability" effects, presumably inductomeric in character, which would lead to the correct order for the halogens. This explanation is not favoured for two reasons. First, it seems inherently more likely that the spectral transitions will be determined largely by what has been called a static (polarisation) effect, unless one is forced to introduce the additional hypothesis of "polarisability" effects. Secondly, since the electromeric effect is reported to be in the order -F > -Cl > -Br > -I, the spectral changes would have to be due to the inductomeric effect.[20] However, inductive effects, which are generally supposed to decrease rapidly, as the distance between the two chromophores increases, would not be the same in the ortho- and para-positions. Yet spectral data indicate, that in the absence of steric effects, spectra obtained from ortho- and para-substituted compounds are similar.

This then points to conjugative, or resonance effects, and in particular to the mesomeric effect as the explanation of the observed changes. This thesis examines some of the implications in assuming the spectral changes to be due to the mesomeric effect, this being in order of magnitude -I > -Br > -Cl > -F.

ULTRAVIOLET ABSORPTION SPECTRA

The main absorption band of halogen-substituted benzoic acids in the ultraviolet region may now be correlated with transitions involving mainly dipolar excited states. These may be crudely represented by structures of type I (illustrating mesomeric effects) and type II (illustrating inductive effects, that is, involving electrostatic influences of the valency electrons of the halogen atom only).



I A I B II A II B

The values for the mesomeric effects thus obtained for halogens and other atoms or groups can then be directly compared with the accepted values, as established by the evidence of dipole moments and chemical equilibria.

By using para-disubstituted compounds, not only are inductive effects minimized but steric

effects are made negligible as a first approximation. There is some evidence for second-order effects under the latter heading,[15] since minor steric effects probably operate even in para-disubstituted compounds, because of the adjoining hydrogen atoms. Under the heading of inductive effects also, a larger number of second-order effects suggest themselves, for example, inductive effects of the halogen atom directly on the carboxyl group or intermolecular inductive effects. However, the argument already has been advanced against inductive effects, namely that since ortho and para-disubstituted benzene derivatives, in the absence of steric effects, have similar spectra,[13] consequently inductive effects must be small. This leads to the conclusion that most of these second-order inductive effects similarly play only a minor part in determining transition energies.

Another argument against the predominance of inductive effects, even in the spectra of meta-disubstituted compounds, is provided by the relevant data of benzoic acids and acetanilides.[16] It is found that in the meta-substituted compound, where the mesomeric effect by definition is small, the spectrum generally resembles that of the parent compound. Consequently, if the inductive effect is of little importance in determining the transition energies of meta-compounds, it seems reasonable to suppose it to be even less for the corresponding para-isomers.

A further reason why induced polarisation may be regarded as small is that in fluoro-substituted compounds, where the inductive effect should be greatest, hardly any change is in fact observed by comparison with the parent compound. (See Table II). This argument is somewhat strengthened by the fact that any steric effect of the fluorine atom is small and thus second-order steric factors cannot readily be postulated to oppose any inductive effects.

It is of interest to note at this stage that similar relationships, namely resemblances between ortho - and para-disubstituted benzene derivatives and between mono- substituted and meta-disubstituted benzene derivatives, are not observed for dissociation constants. This point will be referred to again later.

The relevant spectra in absolute ethanol are collected in Table I. The $\Delta\lambda$ values, where $\Delta\lambda = \lambda_2 - \lambda_1$, and λ_2 and λ_1 represent the locations of maximal absorption of the main absorption bands of para-halogen substituted and parent compounds respectively, are shown in Table II.

Figures I - III and Table II show that mesomeric effects are of approximately the same significance in halogen-substituted benzenes and in para-halogen substituted-benzoic acids, -acetophenones and -benzaldehydes. The slopes of the approximately straight lines

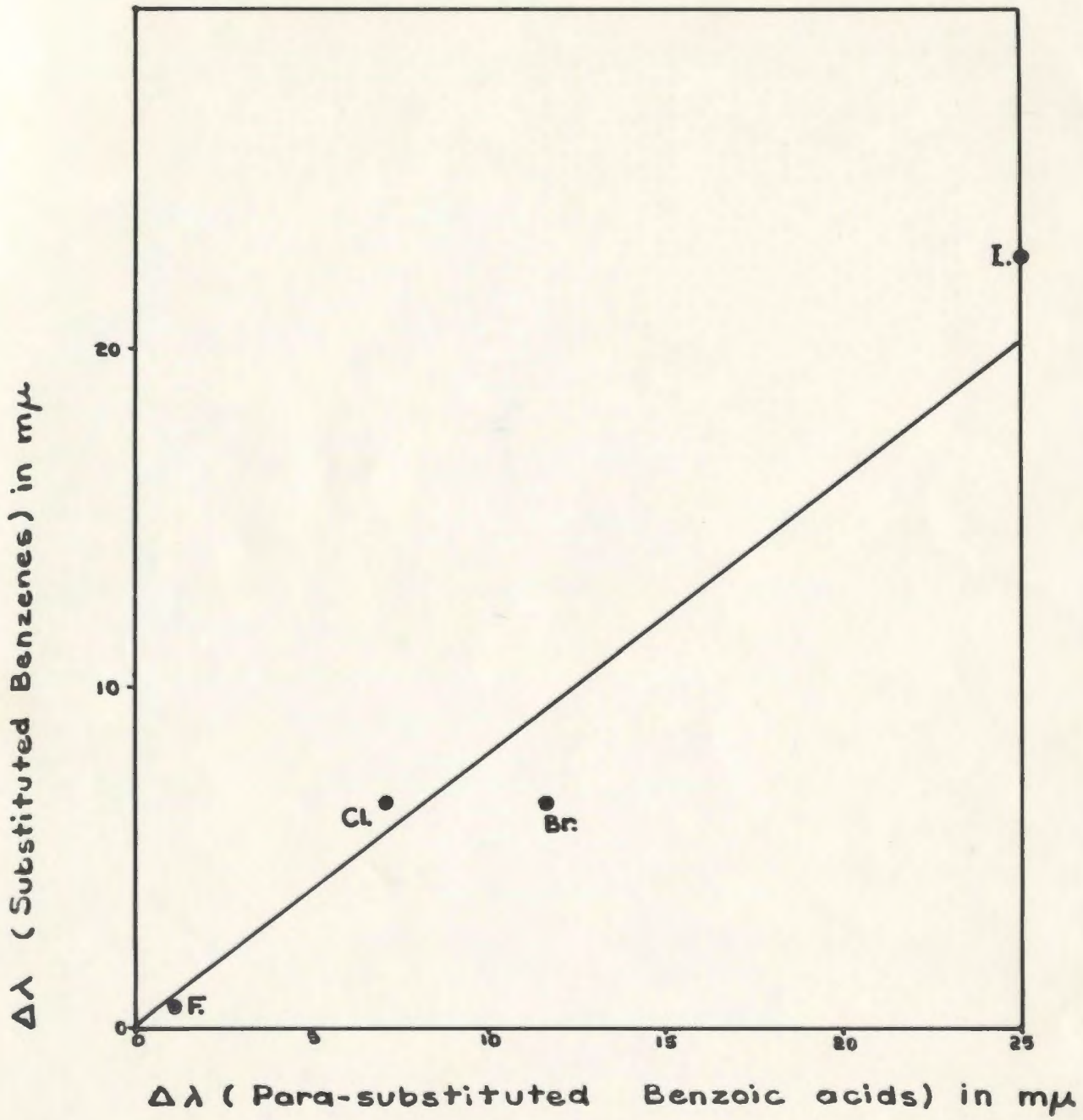

I.
20
10
Cl.
Br.
F.
0
0
5
10
15
20
25
Δλ (Substituted Benzenes) in mμ
Δλ (Para-substituted Benzoic acids) in mμ

FIGURE 1.

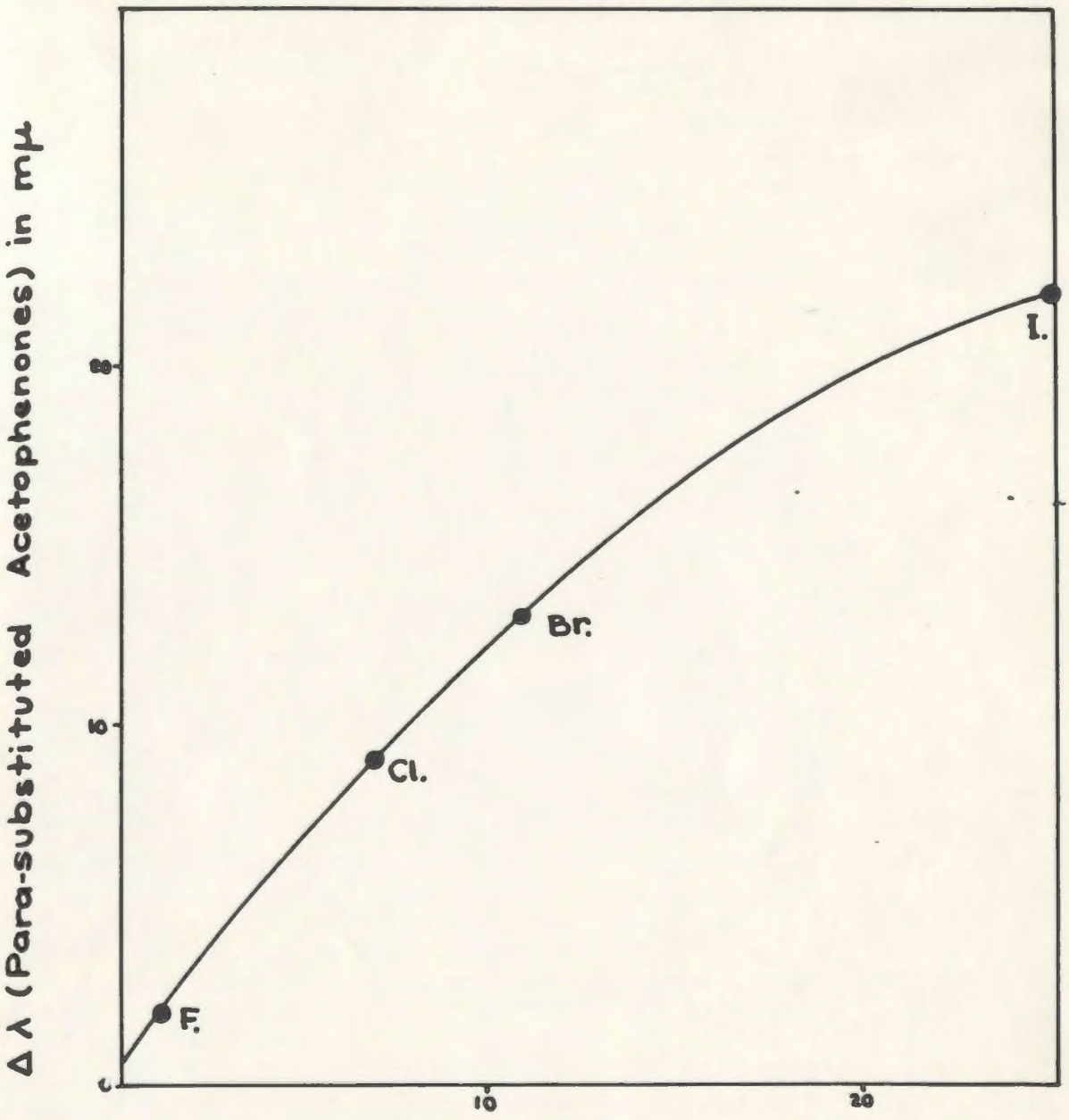

Δ λ (Para-substituted Acetophenones) in mμ
0
5
10
20
F.
Cl.
Br.
I.
Δ λ (Para-substituted Benzoic acids) in mμ

FIGURE 11.

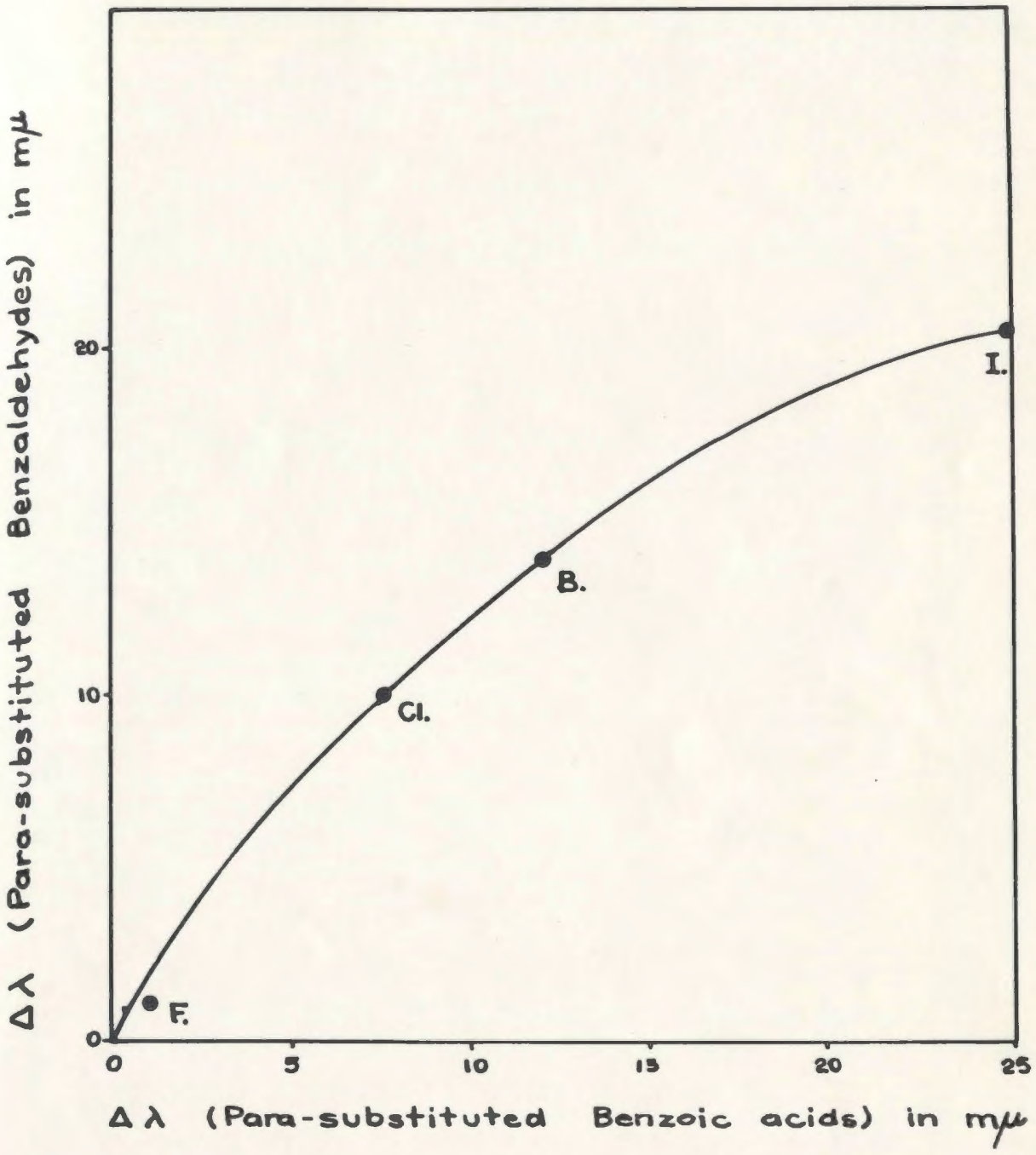

Δλ (Para-substituted Benzaldehydes) in mμ
20
10
0
I.
B.
Cl.
F.
0
5
10
15
20
25
Δλ (Para-substituted Benzoic acids) in mμ

FIGURE III.

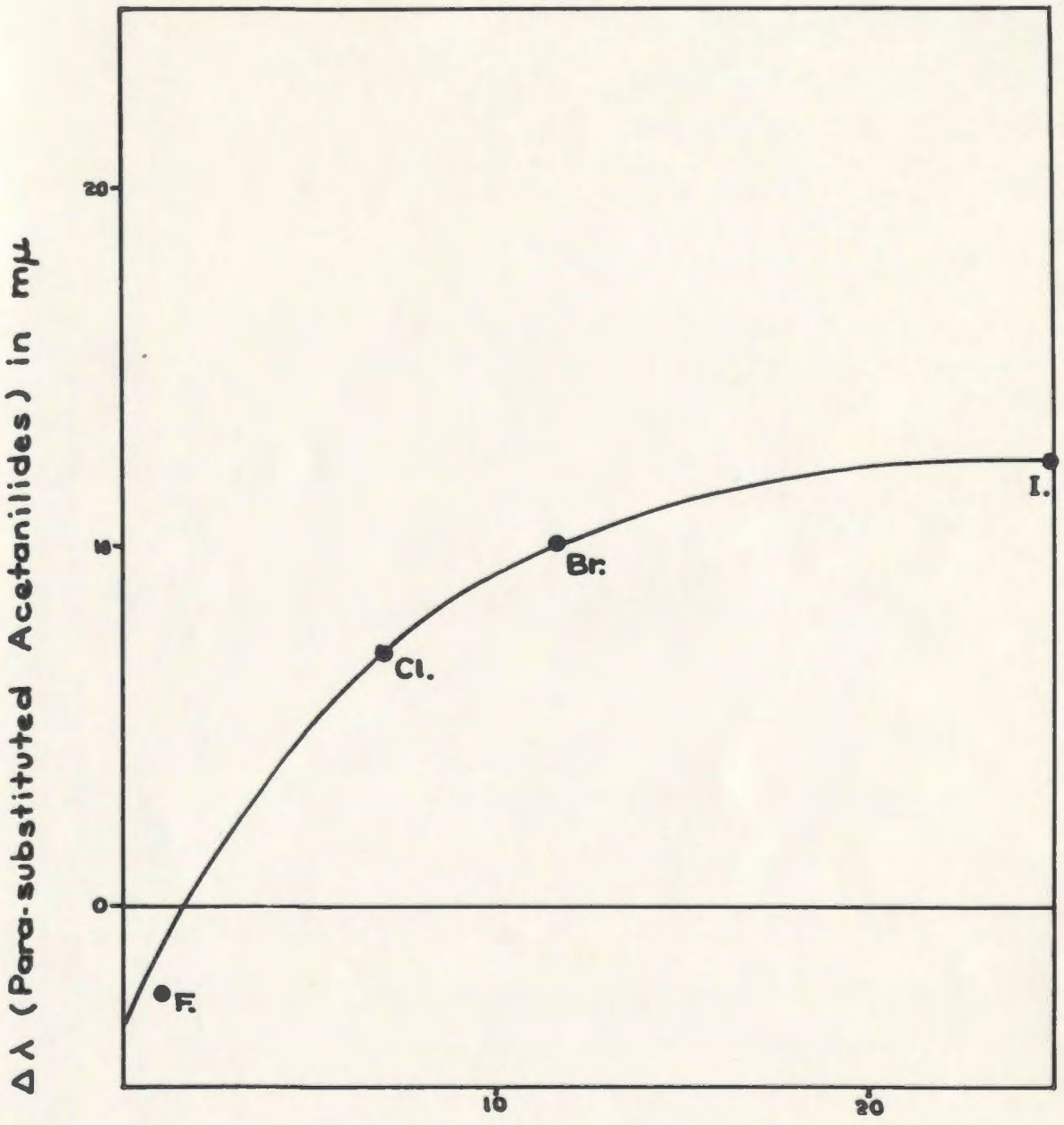

Δλ (Para-substituted Acetanilides) in mμ
20
5
0
F.
Cl.
Br.
I.
10
20
Δλ (Para-substituted Benzoic acids) in mμ

FIGURE IV.

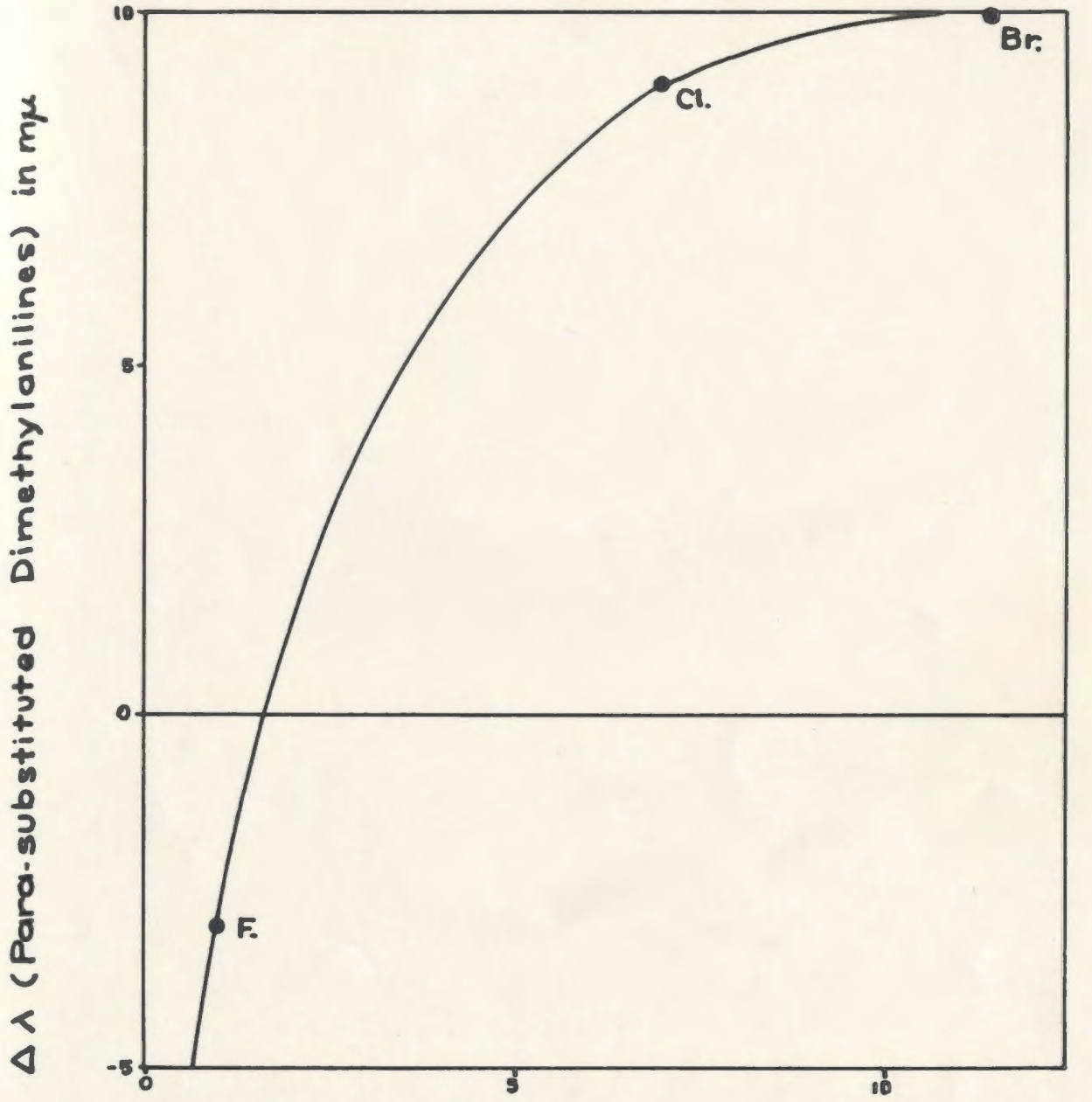

10
5
0
-5
0
5
10
Br.
Cl.
F.
Δλ (Para-substituted Dimethylanilines) in mμ
Δλ (Para-substituted Benzoic acid) in mμ

FIGURE V.

TABLE I

MAXIMA ($m\mu$) OF B-BANDS OF COMPOUNDS

p-R.C_6H_5X

X =	H		F		Cl		Br		I	
R	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$-COOH_6$ (16)	227	11,000	228	11,000	234	15,000	238.5	16,000	252	17,000
-H (4,11)	203.5	7,400	204	6,200	210	7,500	210	8,600	226	13,000
$-NHCOCH_3$ (16)	242	14,500	240	13,000	249	18,000	252	18,500	254	23,000
$-N(Me)_2$ (24)	250	13,600	247	12,300	259	17,000	260	19,600	–	–
$-COCH_3$ (18)	240	12,500	242	9,000	249	16,000	253	16,000	262	16,000
-CHO (15)	244	13,000	245	12,000	254	15,000	258	18,000	265	18,500

TABLE II

$\Delta\lambda$ VALUES IN $m\mu$ FOR PARA-HALOGEN SUBSTITUTED COMPOUNDS DESCRIBED IN TABLE I

X =	F	Cl	Br	I
R				
-COOH	1	7	11.5	25
-H	0.5	6.5	6.5	22.5
$-NHCOCH_3$	-2	7	10	12
$-N(Me)_2$	-3	9	10	–
$-COCH_3$	2	9	13	22
-CHO	1	10	14	21

thus obtained are about 45°, indicating equal displacements for the above-mentioned compounds due to mesomeric effects. The corresponding acetanilides and N,N-dimethylanilines compared to benzoic acids generally suggest slopes initially greater than 45°, but flattening out considerably towards the larger iodine-atom (Figures IV and V).

A tentative interpretation of these observations may now be made as follows. The mesomeric effect is caused in benzoic acids, benzaldehydes and acetophenones primarily by the halogen atom, in the presence of a nitrogen-atom, because of its unshared electrons, additional conjugation enhances the congestion of electrons in the para-positions and this causes:

(I) A greater mesomeric effect, since the effect is now able to operate more extensively. (It will be shown later that there are strong indications that the mesomeric effect operates preferentially in excited states of type IA and I B.)

(II) Second-order Steric effects to increase, due to interaction of the halogen atom with the now increased electron density. This becomes appreciable with the bulky iodine atom and causes an anomalously low value for p-iodo-N,N-dimethylaniline.

It may be noted that in Table II and Figures I - V, wave-length changes rather than changes in the observed intensities have been chosen as the measure of electrical effects. Although both give the correct order, since the increased mesomeric effect also gives rise to increased transition probability, wave-length changes are more conveniently converted into energy values. Further there is evidence that values of transition probabilities as measured by the absorption intensity (ε) are more susceptible to small steric effects.[13,14]

Another recent interesting example has been provided by the spectra of 2- halogen-substituted 4-methoxy-4'-methyldiphenyls. (See Table III).

TABLE III

MAXIMA ($m\mu$) OF B-BANDS OF COMPOUNDS p-MeO.C_6H_4.C_6H_4.CH_2X ACCORDING TO BURAWOY AND SPINNER,[8] AND $\Delta\lambda$ VALUES FOR THESE AND PARA-SUBSTITUTED BENZOIC ACIDS

X	λ	ε	$\Delta\lambda$	$\Delta\lambda$ (Benzoic Acids)
H	260	23,600	0	0
Cl	271	23,000	11	7
Br	277	23,500	17	11.5
I	291	23,500	31	25

Although Burawoy and Spinner[8] explain the spectral changes by the "polarisability" of substituents, the spectra of the diphenyls fit in with the assumptions made in this thesis. The $\Delta\lambda$ changes of the diphenyls are proportional to other $\Delta\lambda$ changes already described and hence to the proposed mesomeric effects. This example also emphasises the advantages of considering wave-length changes rather than absorption intensities, since here the intensities are fairly close together, presumably because of the high initial absorption intensity. The example finally reinforces the assumed steric hindrance of the iodine atom since the iodine atom in 2 - iodo- 4-methoxy -4' -methyl-diphenyl is separated by a methylene-group from the phenyl group, consequently causing considerably less steric interaction.

In accordance with the hypothesis, the steric effect associated with high electron densities around the halogen atom is no longer observed, and the $\Delta\lambda$ value for the iodo-compound concurs with the expected value.

DIPOLE MOMENT DATA

The mesomeric electron release by halogen atoms was first assumed by Ingold to be in the order -I > -Br > -Cl > -F.[19] This order, which was initially supported by the mesomeric moments of the halogen-substituted benzenes was later reversed because of further studies by Groves and Sugden[18] and by Audsley and Goss.[1]

Dipole moment data, as a method of determining mesomeric effects, have the inherent disadvantage that assumptions must be made with regard to a reference compound, in which no mesomeric effect operates. For example, halogen atoms attached to a methyl and a tertiary butyl group have both been used as reference compounds.

TABLE IV

COMPARISONS OF DIPOLE MOMENTS USED IN THE DETERMINATION OF MESOMERIC EFFECTS, AND THE ACTUAL MESOMERIC MOMENTS THUS OBTAINED.

X	Bu^tX	MeX			PhX			DIFFERENCES CORRESPONDING TO MESOMERIC EFFECTS		
	(26)	(20)	(18)	(1)	(26)	(18)	1	(26)	(18)	(1)
-F	-	-1.81	-2.61	-2.48	-	-1.61	-1.44	-	+ 1.00	+ 1.04
-Cl	-2.15	-1.83	-2.70	-2.59	-1.70	-1.73	-1.64	+ 0.45	+ 0.97	+ 0.95
-Br	-2.21	-1.82	-2.60	-2.42	-1.55	-1.71	-1.68	+ 0.66	+ 0.89	+ 0.74
-I	-2.13	-1.48	-2.37	-2.20	-1.35	-1.50	-1.69	+ 0.78	+ 0.87	+ 0.51

As may be noted from the data collected in Table IV there is considerable difference between the values of the two compounds, and also between those and others used for reference purposes (see Table IV). Actually, these differences of the dipole moments, with just one exception, (see below) are at least of the same order as the differences between them and the benzene derivatives, namely the difference on which the calculation of mesomeric moments is in fact based. Although it may be assumed, for example, that the tertiary butyl halide is a more appropriate compound than the methyl halide for comparison purposes, just how much better a comparison compound it actually is, can hardly be ascertained with any great degree of accuracy. This follows because firstly, it seems doubtful that the possibilities of induced polarisation in bonds adjacent to R-X, are nearly equal when R is tertiary-butyl or phenyl. Secondly, second-order steric effects, which may be appreciable for tertiary-butyl compounds, particularly the iodide, have been neglected; this, for example, may affect the shape of the radical and thus alter induced moments. Thirdly, some of the data apparently lack correction for solvent effects, which have been shown to be appreciable.

Hence, the variety of results obtained for the mesomeric effect of the halogens is perhaps

not surprising. As it is, the initial comparisons based on methyl halides yield random results for the order of mesomeric moments, which may be further varied, depending upon whether the moments are determined in the gaseous state or in solution.[20,27] If tertiary-butyl halides are used as comparison substances, the proposed order is in fact obtained, that is, the mesomeric moments are in the order -I > -Br > -Cl.[26] However, for the reasons given above, one would not expect to obtain precise agreement between the values of the mesomeric effects thus obtained and those obtained from spectral data. It may be regarded as somewhat fortuitous that the same order for the halogens is obtained by both methods. Groves and Sugden[17] have later obtained some values for the mesomeric moment in a different order (-Br > -F > -Cl), but the reported differences were quite small (within 0.06 Debye units between the extreme values).

Later still, Groves and Sugden[18] have obtained some values in the reverse order (-F > -Cl > -Br > -I), but since the difference between the extreme values is only 0.13 Debye units this again, for the reasons given above, can hardly be taken as a complete proof for the accepted order of mesomeric effects. It is perhaps significant that no attempt was made in this, or the paper cited below, to estimate the percentage error for the

values used in obtaining the mesomeric moments. It should be remembered in this connection, that the mesomeric moment is obtained indirectly from two values, the degree of error in both being uncertain.

Probably the most recent paper which has reported values on mesomeric moments of halogens from dipole moment is one by Audsley and Goss,[18] which again concludes that the order for the halogens is the reverse of the one here proposed. The differences are much larger than earlier values, yet it must be noticed that these latter ones are obtained from solution data. Thus, quite apart from previous objections, it seems that the applied solvent corrections account very largely for the new values, compared for instance, with the vapour phase data of Groves and Sugden. It somehow seems difficult to visualise a mesomeric moment which shows so great a difference in the liquid and gaseous phases. This difference is considerably higher for the bromo and iodo compounds than for the other halogen compounds. (See Table IV). It is perhaps unfortunate that at the time the -F> -Cl> -Br> -I order for the mesomeric effect had been considered established.

From the evidence stated it may be concluded that while dipole moment data provide an

excellent method of determining inductive effects and provide evidence for the existence of mesomeric effects, which for halogen atoms oppose the inductive effects, they seem to provide a less satisfactory method for determining accurate values of mesomeric effects than do the data from light absorption. Dipole moment data are lastly of interest since they support the hypothesis of a variable mesomeric effect, as was evidenced in light absorption data, from the greater range of wavelength changes in the acetanilides and N,N-dimethylanilines compared to benzoic acids and benzenes. This same effect was qualitatively demonstrated from dipole moment data by Bennett and Glasstone[2], who showed that the observed moments of phenols, anisoles and anilines were invariably greater than the values calculated from vector addition.

STRENGTH OF ACIDS AND BASES

Acid and base dissociation constants, as is well known, may also be used as evidence for mesomeric effects, in addition to providing a measure of inductive effects. The relevant constants are listed in Table V and it will be noticed that the values are in a different order from that obtained from the data on B-band of the ultraviolet light absorption spectra.

At first sight[13,14,16] it would appear - using the benzoic acids as typical examples, although the arguments would apply equally well to the other compounds listed in Table V - that the inductive effect is of considerably greater importance in determining acidity and basicity constants than in light absorption data. Throughout the series, the ortho-substituted compounds exhibit much larger acidity constants than the meta-compounds, and these in turn are larger than the corresponding para-isomers. This is a clear indication of the preponderance of inductive effects but unfortunately more than one variable determines the obtained values, as is readily shown by a somewhat more detailed analysis.

By a comparison of ortho-compounds where the inductive effect is largest, it is noted that o-fluoro-benzoic acid exhibits a much larger acidity constant than the parent compound. Since the inductive effect

TABLE V

ACIDITY AND BASICITY CONSTANTS FOR HALOGEN-SUBSTITUTED AROMATIC ACIDS AND BASES (AFTER INGOLD)[20]

POSITION	H	F	Cl	Br	I
(A) Benzoic Acids: 10^5 Ka in Water					
ortho-	6.27	54.1	114	140	137
meta-	6.27	13.6	14.8	15.4	14.1
para-	6.27	7.22	10.5	10.7	
(B) Benzoic Acids: 10^5Ka in 50% aqueous MeOH					
ortho-	0.513	6.61	7.08	7.08	6.6
meta-	0.513	1.41	1.45	1.35	1.41
para-	0.513	0.832	1.00	0.933	1.00
(C) Phenylboronic Acids: 10^{10} Ka in 25% aqueous EtOH					
ortho-	1.97		14.0		
meta-	1.97	11.0	13.5	14.6	
para-	1.97	3.66	6.30	7.26	
(D) Phenols: 10^{10} Ka in 30% aqueous EtOH					
ortho-	0.32	4.27	10.2	9.78	9.12
meta-	0.32	1.51	4.90	4.37	3.89
para-	0.32	0.26	1.32	1.55	2.19
(E) Anilines: 10^{12} K_b in 30% aqueous EtOH					
ortho-	126	2.95	1.35	1.00	0.36
meta-	126	10.5	8.51	7.94	7.59
para-	126	120	28.8	21.9	15.1

apparently increases the acidity, this should be proportional to the inductive effect, that is, in the order -F > -Cl > -Br > -I. This is not the order obtained. In fact, in passing from -F to -I, the acidity is increased (see Table V). The reverse order cannot be explained solely in terms of an opposing mesomeric effect since this effect, as judged from the values of the para-isomers, is hardly adequate to account for the above changes.

Steric factors will certainly play a part, as is clearly evidenced from spectral data, and these may account for larger dissociation constants[13,14,16] as the halogen atom increases in size. This is hardly the complete explanation because solvent effects must surely play an appreciable part as witnessed by the different orders (of the halogens) obtained in different solvents (Table V, (A) and (B) - benzoic acid in water and 50% aqueous methanol)

Consequently, ortho-substituted compounds do not at present lend themselves to a more detailed analysis. Meta-isomers may be expected to be more suitable, since there the mesomeric effect will be small and steric factors also ~~would~~ will be of considerably less significance. However, again there is no clear indication that the obtained values are in the order of the inductive effects.

For para-isomers, first-order steric effects ~~would~~ will be small, and it may be assumed tentatively, that the mesomeric effects will predominate. Certainly, a definite order of the halogens becomes apparent. Now, one can either assume with Bettman et al, that the mesomeric effect weakens the acid[3,20] (that is, the effect is to be associated primarily with dipolar excited states of type 1 B), which would give an order for the acid-weakening of -F> -Cl> -Br> -I; or one may surely also assume that the mesomeric effect strengthens the acid (that is, the effect is to be associated primarily with excited states of type 1 A). This places the acidity constants in the same order as the one here proposed for the mesomeric effects.

Two indications favour the latter hypothesis. Firstly, since the substitution of ~~flourine~~ halogen for hydrogen in para-substituted compounds generally strengthens the acid (see Table V), it would seem that the mesomeric effect does give rise to an increased acidity. There is one exception to this: the acidity constant of p-fluorophenol actually shows a small decrease. This is used by Ingold in support of his hypothesis of an acid-weakening[20] disturbance because of the mesomeric effect, which

as expected is strongest for fluorine. However, another explanation of this observation seems possible. The mesomeric effect of the fluorine atom is small. This view receives support from light absorption data, where it was shown (see Table I) that the spectrum of the fluorine compound frequently resembles that of the parent. It may also be noted (see Table II) that the wave-length shift, due to the fluorine atom is sometimes negative, possibly because the halogen atom, before exerting its mesomeric effect, must first overcome opposing effects of the other substituent. A similar effect may therefore account for the anomalous dissociation constant of p-fluorophenol (see also next section.) A second indication in favour of the argument, arises from the graphs, which show reasonably good agreement between the changes due to mesomeric effects obtained from acidity constant data and those from light absorption data.

On plotting $\lambda\Delta$ values against values of the acidity constants, it is noted that similar curves are obtained, namely, initially almost straight lines with a distinct "bending" or "flattening-out" towards the iodine value. This "flattening-out" has been ascribed previously to second-order steric factors and an analogous

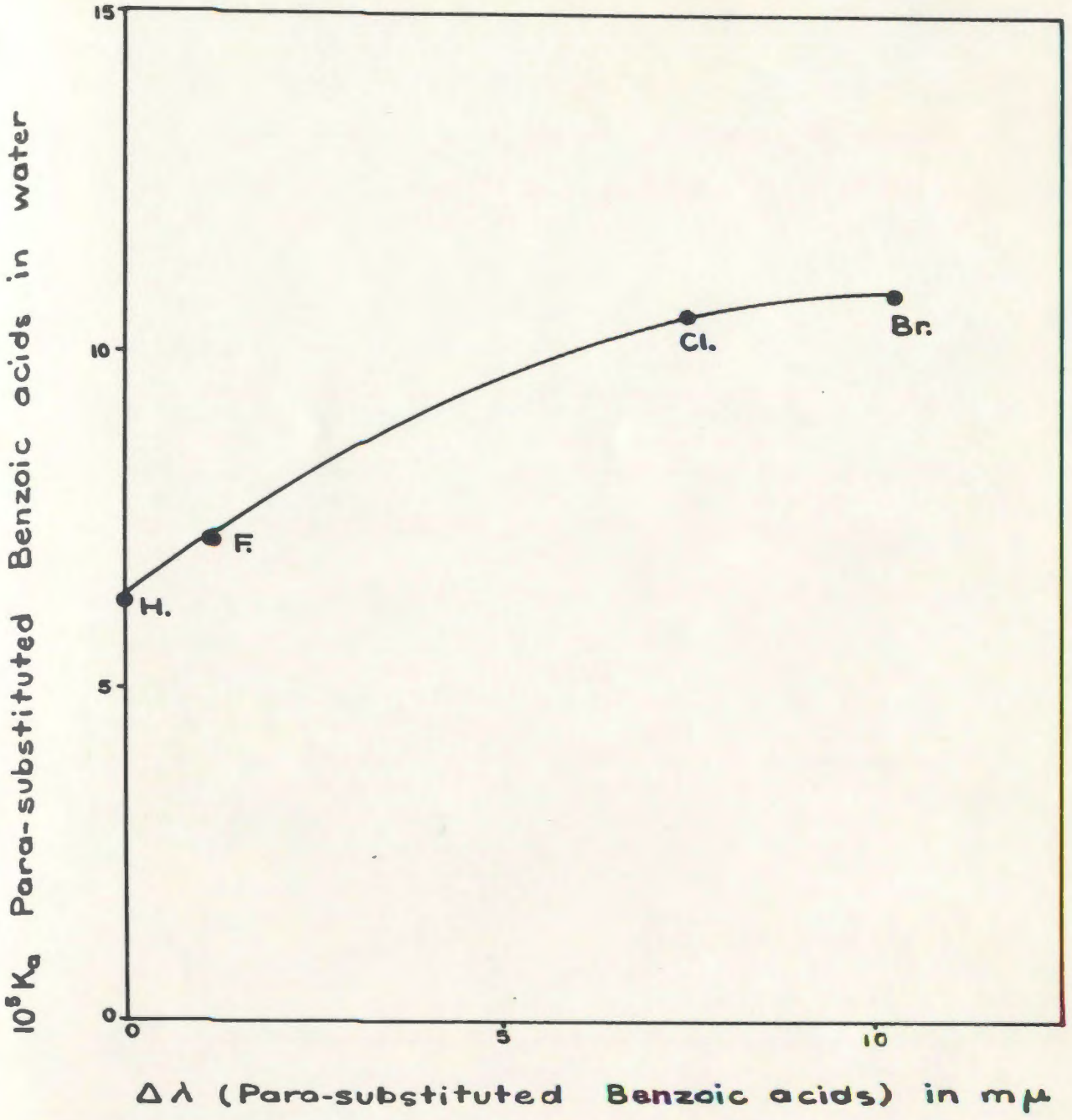

15
10
5
0
0
5
10
H.
F.
Cl.
Br.
$10^5 K_a$ Para-substituted Benzoic acids in water
$\Delta\lambda$ (Para-substituted Benzoic acids) in mμ

FIGURE VI.

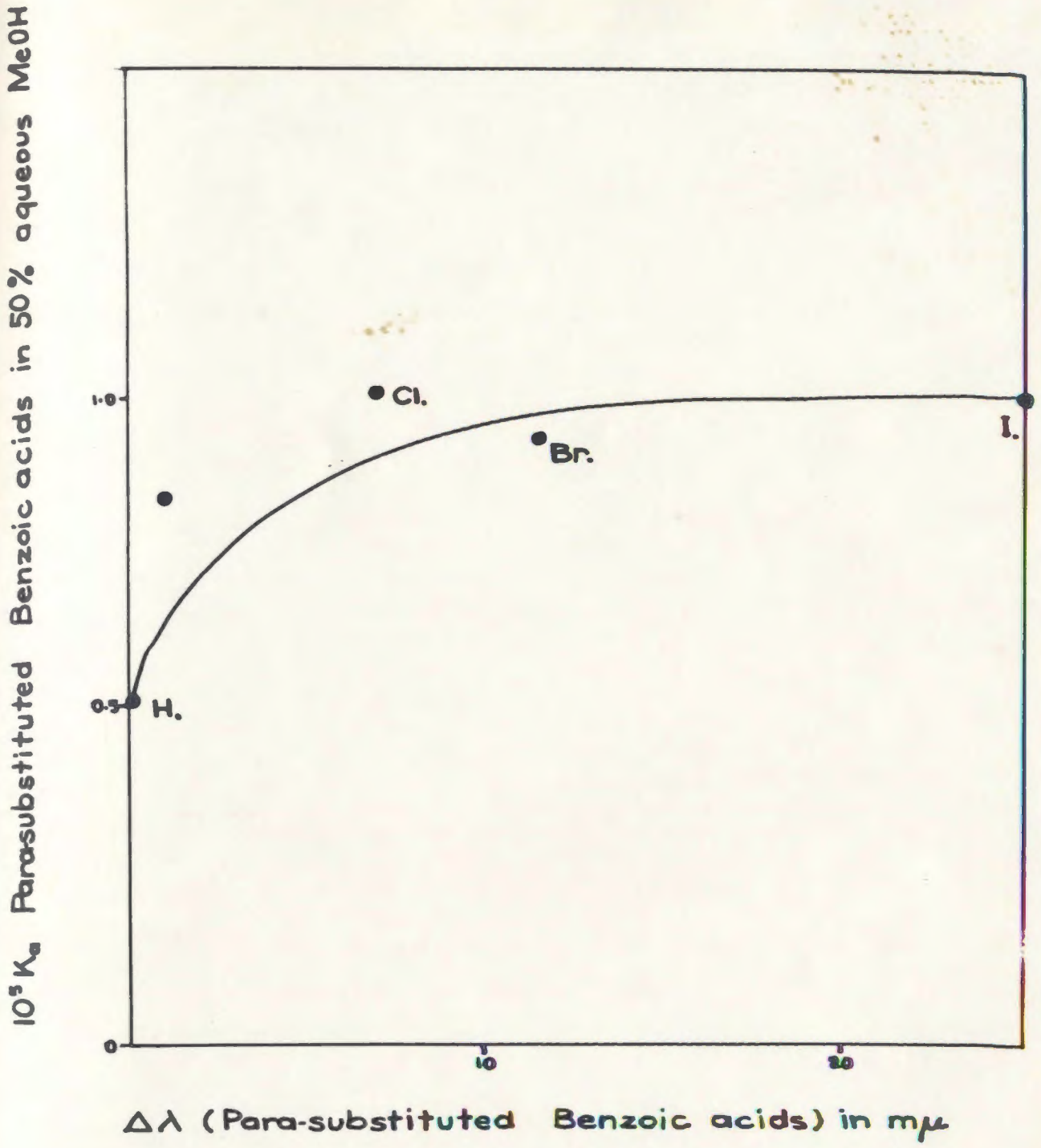

$10^5 K_a$ Parasubstituted Benzoic acids in 50% aqueous MeOH
1·0
0·3
0
Cl.
Br.
I.
H.
10
20
Δλ (Para-substituted Benzoic acids) in mμ

FIGURE VII.

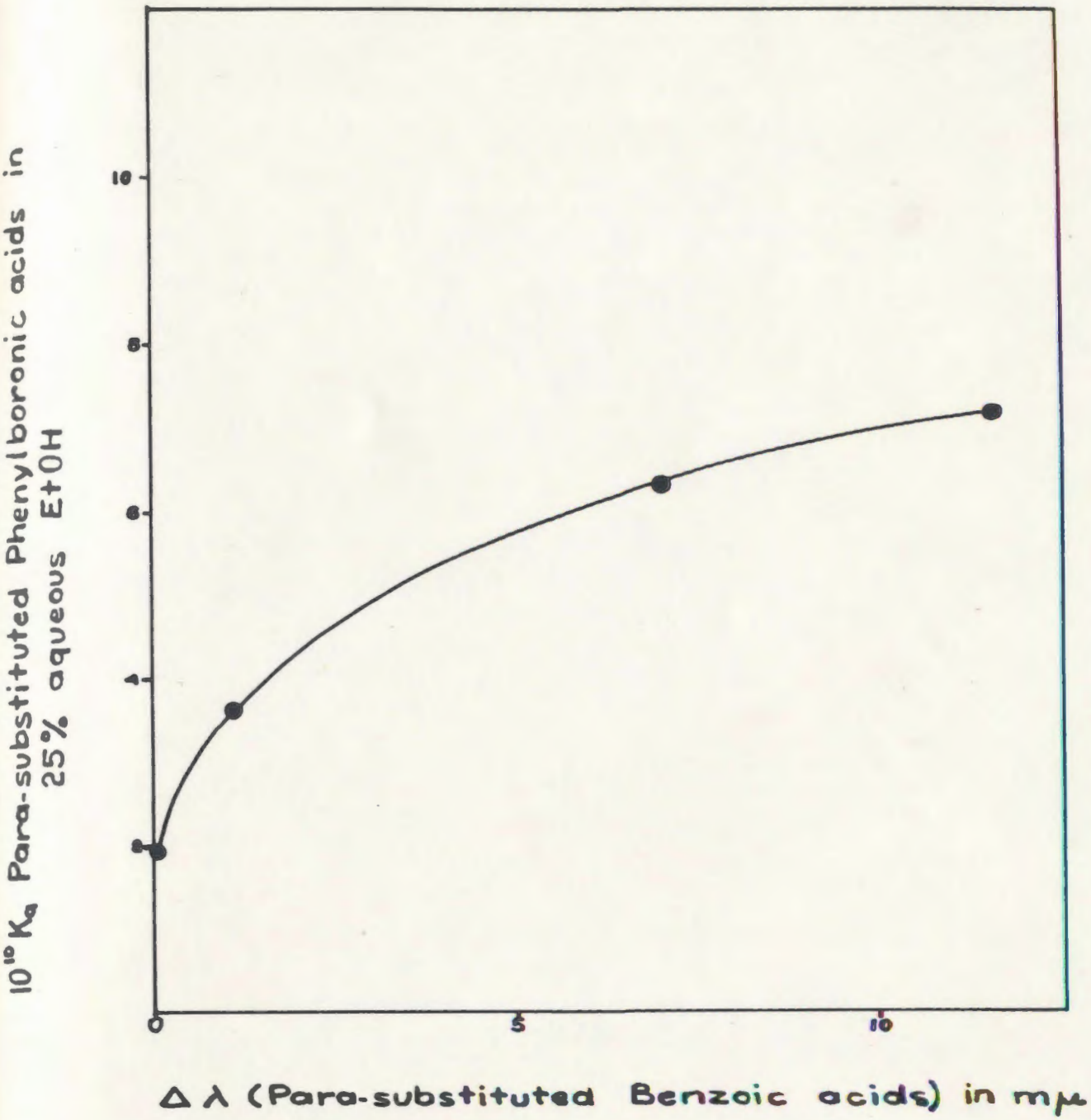

$10^{10} K_a$ Para-substituted Phenylboronic acids in 25% aqueous EtOH
10
8
6
4
2
0
5
10
Δ λ (Para-substituted Benzoic acids) in mμ

FIGURE VIII.

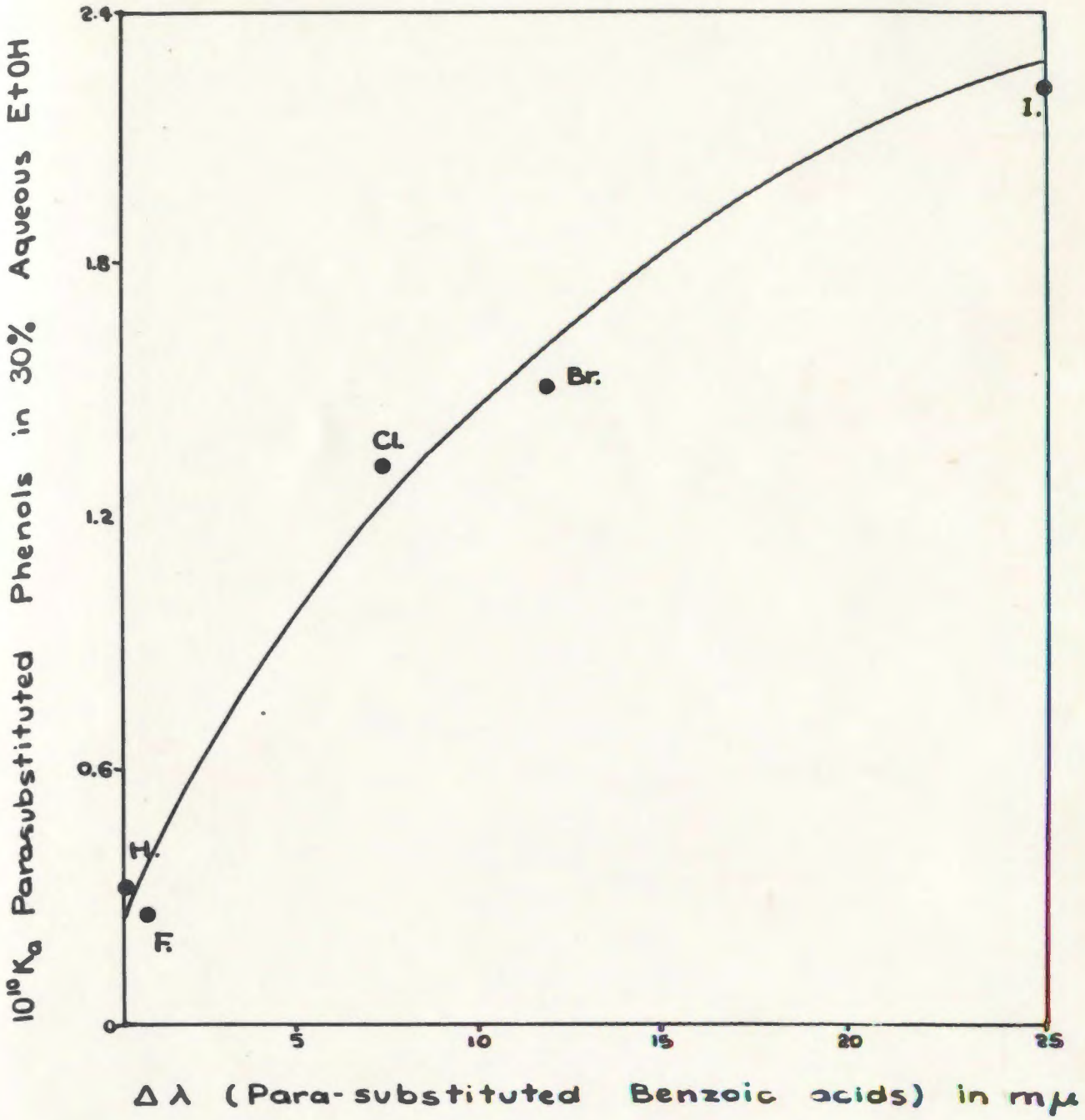

2.4
1.8
1.2
0.6
0
5
10
15
20
25
H.
F.
Cl.
Br.
I.
$10^{10} K_a$ Parasubstituted Phenols in 30% Aqueous EtOH
Δλ (Para-substituted Benzoic acids) in mμ

FIGURE IX.

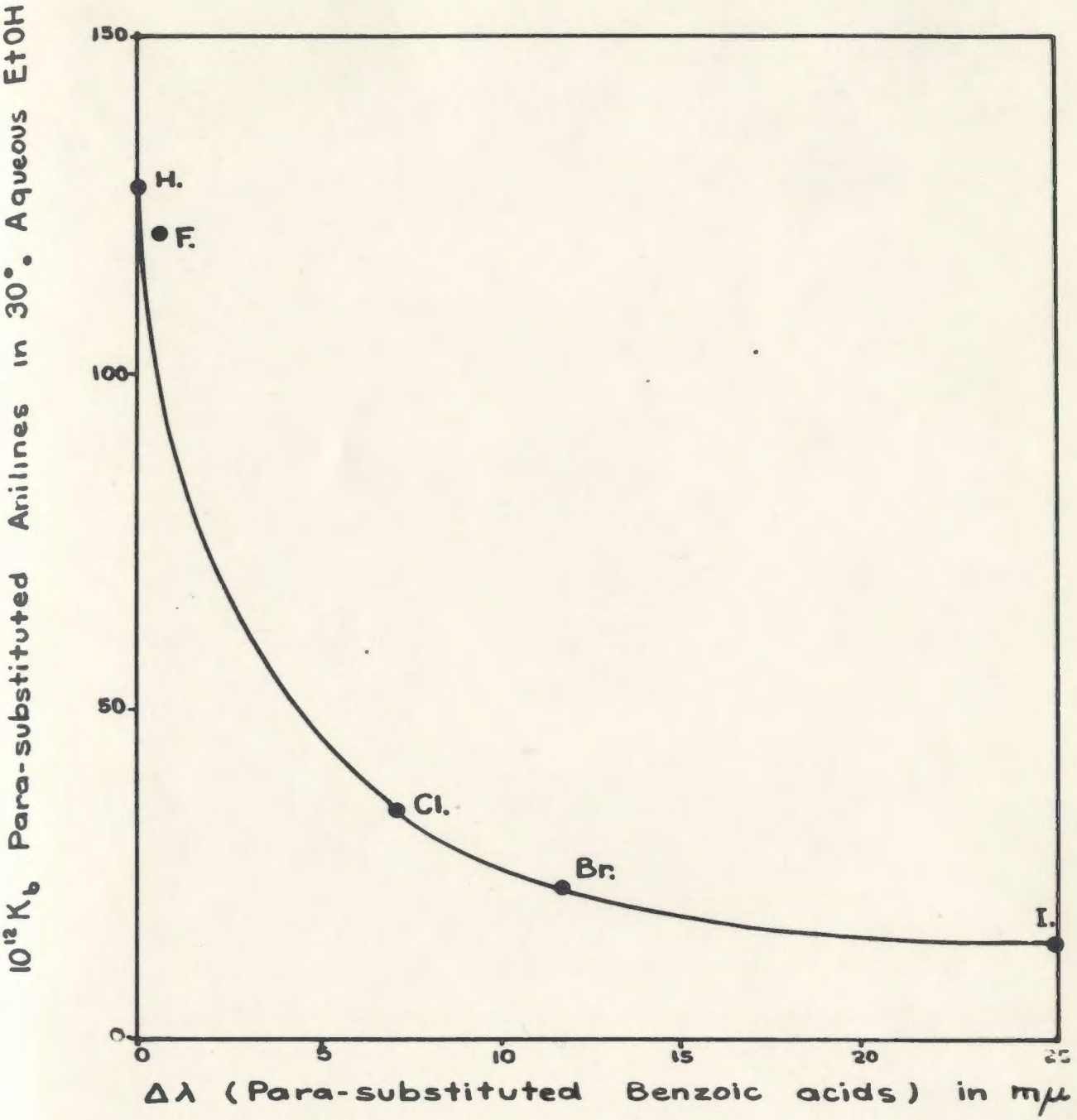

$10^{12} K_b$ Para-substituted Anilines in 30°. Aqueous EtOH
150
100
50
0
H.
F.
Cl.
Br.
I.
0
5
10
15
20
25
Δλ (Para-substituted Benzoic acids) in mμ

FIGURE X.

interpretation is proposed for the effect in this instance. This would suggest that acidity-constants are more susceptible to steric effects than are the light absorption spectra, an observation which will be referred to again in the section (see below).

To sum up, it may be noted, that in comparing acidity and basicity constants, mesomeric effects again become evident, as second-order effects relative to inductive effects, and that a satisfactory correlation of the constants may be made on the assumption that the mesomeric effects vary in the order -I> -Br> -Cl> -F and increase the acidity. Also it appears that the dissociation constants, compared with dipole moment data may be regarded as a more reliable measure of mesomeric effects, and finally that steric factors appreciably affect the values obtained.

SOME THEORETICAL OBSERVATIONS

It may now be concluded that neither dipole moment data nor equilibrium constants are ideally suited to give absolute or even reliable orders for mesomeric effects. Both give roughly correct correlations between the mesomeric values thus obtained, and the ortho-, para-, or meta-directing properties of the substituents, and equilibrium constant data further show fairly exact correlations with the data obtained from spectra. However, the approximate nature of the results must be remembered. Also noteworthy, is the consideration that reaction rate constants are even less likely to yield accurate values of mesomeric effects, since the interaction of two or more molecules will introduce additional variables. Nevertheless, the following conclusions seem to emerge from the data presented so far:

1. Information indicating the existence and relative magnitude of mesomeric effects can be obtained from reaction rates, dipole moment data, equilibrium constants, light absorption data and other physical constants. Whether the mesomeric effect involves a disturbance of electrons from one atom to another, as has been proposed in the classical conception of mesomerism, or merely an inductive

displacement, as has been suggested by Burawoy and others, (cf. (8) and references quoted there) perhaps cannot be decided upon conclusively. If however, the latter hypothesis is so formulated as to suggest a decreased interaction as the distance between the chromophores increases - and so predict a dissimilarity in ortho- and para-substituted compounds - it must be deemed the less satisfactory explanation of the observed phenomena. Some recent theoretical examinations on spectral properties of alkyl-substituted compounds also suggest that energy shifts resulting from <u>inductive</u> effects alone will be positive, thus leading to hypsochromic shifts. Therefore it may be tentatively concluded [9,10] that whenever an overall bathochromic shift occurs, the bathochromic shift due to the <u>mesomeric</u> effect must be of larger magnitude than any <u>inductive</u> effect.

2. It seems an unjustified assumption to associate the <u>mesomeric</u> effect in different compounds with one and the same dipolar excited state. For example, while one particular dipolar excited state, such as 1 A, may well be associated with the <u>mesomeric</u> effect in certain compounds, other dipolar structures, such as 1 B, may become more important on the introducing of other substituents.

This suggestion appears to be supported by equilibrium constants of para-substituted acids, where sometimes a mesomeric effect produces an acid-weakening, (cf. para-methyl substituted acids - Ingold) while at other times it appears to act in the opposite manner (see previous section). An interesting related effect has recently been described for spectra of substituted benzaldehydes and acetophenones. There, the para-methyl group reduced steric interaction in 2, 4, 6 - trimethylbenzaldehyde and 2, 4 - dimethylacetophenone, but increased it in 2, 4, 6 -trimethylacetophenone.[5] This phenomenon was ascribed to additional conjugation, either overcoming or further enhancing steric interactions already present. This explanation may also be used to relate two other phenomena previously referred to in this thesis. First, it was noted that slight steric interactions, of the type postulated in chemical equilibria, do not show up as well in light absorption properties (see Figures VI - X). This may be because light absorption properties involve, to a larger extent, excited states in which the slight steric hindrance is more readily overcome. Secondly, it was observed in some cases, that a fluorine-substituted compound, with respect to the parent compound, causes a slight negative

wave-length shift (see Table II). It may be noted that, in one instance, a similar effect was also found for acidity constants. This negative shift, may now be explained by saying that the halogen atom first has to overcome the tendency of the nitrogen atom to supply electrons to the benzene-ring. This tendency again is more pronounced in excited states and results in, at first a positive energy displacement (hypsochromic shift), until the positive mesomeric effect becomes sufficiently large to lower again the potential energy of the excited state.

3. The relative importance of mesomeric effects appears to be quite different, in properties like dipole moment and acidity instants data on the one hand, and in light absorption properties on the other. The chief difference between the two sets of properties appears to be that only light absorption data involve transitions to excited states, which are largely dipolar in character. Because of the nature of these excited states, one would expect them to be more susceptible to mesomeric effects. Consequently, the apparent preponderance of mesomeric effects in light absorption data of the halogens - as evidenced from the observed wave-length changes in conjunction with the proposed order of mesomeric effects, and also from the identity of some ortho- and para-isomers -

is perhaps not surprising.

It may therefore be postulated that mesomeric effects are only of secondary importance in ground states and that the potential energy levels of ground states for the halogens are roughly equal (cf. dipole moment data and dissociation constants). Further, mesomeric effects will predominate in excited states and it is suggested that the representation of the transitions involved is approximately as shown in Figure XI.

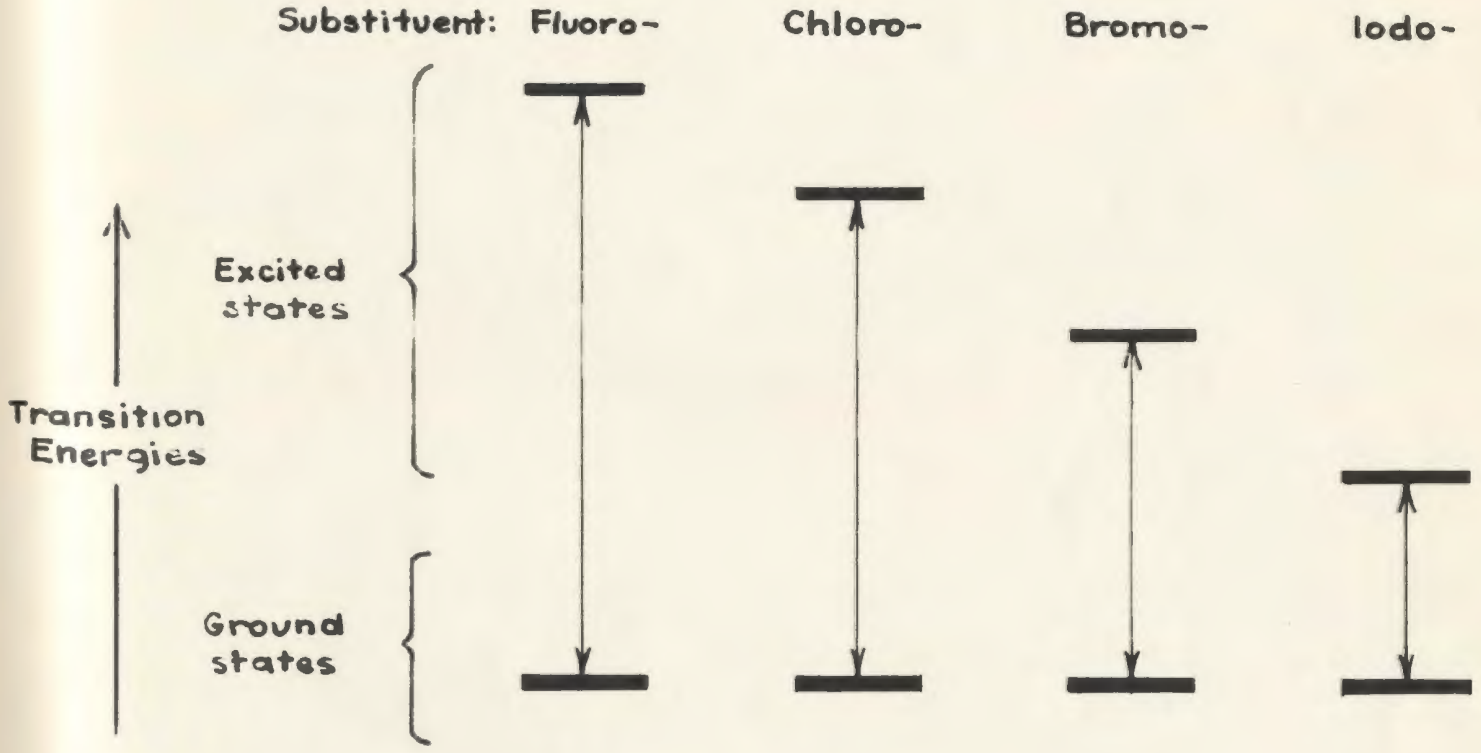


FIGURE XI.

Schematic representation of transitions in para-halogen benzoic acids after Braude and Waight. (6)

Figure 3 illustrates why the mesomeric effect is readily identified in light absorption data, and why it is much less easily identified from dipole moment data and acid dissociation data.

4. Although it is questionable how a knowledge acquired about mesomeric effects in the excited-state is applicable to ground-states and vice versa, a simple semi-quantitative interpretation of mesomeric effects is attempted. Thus it may be hoped, that when the percentage of dipolar forms in the excited- and ground-states have been calculated, it will be possible to obtain measures of the mesomeric effects in various ground states.

In the meantime, the wave-length changes for halogen-substituted benzenes and para halogen-substituted benzoic acids have been used to evaluate the approximate energy gains associated with mesomeric effects in these compounds. These values are recorded in Table VI. It may be noted, that on the basis of very simplified calculations, the change in dipole moments from fluoro- to iodobenzenes due to mesomeric effects, according to the values reported by Groves and Sugden (the latest available gas values) amount to an energy change of approximately 3 kcals/mole.[18] This, as expected, is much less than the value obtained from Table VI (approximately 14 kcals/mole).

TABLE VI

APPROXIMATE POTENTIAL ENERGY GAINS (IN KCALS/MOLE) IN THE PHOTO-EXCITED STATE OF HALOGEN-SUBSTITUTED BENZENES AND BENZOIC ACIDS DUE TO MESOMERIC EFFECTS.

SUBSTITUENT	WAVE-LENGTH CHANGES IN mμ (See Table II)		APPROXIMATE ENERGY GAIN (IN KCALS/MOLE)
	Benzoic Acids	Benzenes	
-F	1	0.5	0.5
-Cl	7	6.5	3
-Br	11.5	6.5	6
-I	25	22.5	15

MESOMERIC EFFECT OF ALKYL SUBSTITUENTS

In the light of the above-mentioned observations, it proved of interest to apply these to the spectra of alkyl-substituted compounds. There also, interpretation of the spectra are not entirely unambiguous.

For alkyl substituents in the *para* position, it has been shown, that bathochromic shifts, although small, in substituted acetophenones are in the order $-Bu^t > -Pr^i > -Et > -Me$. This represents the order of their *inductive* effects rather than the accepted order of their *mesomeric* effects. It consequently suggests that *inductive* effects are of greater importance in these types of compounds. This explanation has been accepted by Burawoy and co-workers[7,8] and others.

The spectra of a number of such alkyl-substituted compounds are collected in Table VII.

It is seen from Table VII, that the changes from methyl to t-butyl cannot readily be ascribed to *mesomeric* effects alone. Although the *mesomeric* effect may account very largely for the change due to the methyl group, it is not sufficiently different from methyl to t-butyl

TABLE VII

MAXIMA ( ) OF B-BANDS IN COMPOUNDS p-R.C_6H_5 X.

X / R	H λ	H ε	Me λ	Me ε	Et λ	Et ε	Pr^i λ	Pr^i ε	Bu^t λ	Bu^t ε
-COOH	227	11,000 16	236	14,000 16					237.5	16,290 25
-H	203.5	7,400 11	206.5	7,000 11			207	8,700	206.5	8,900
$-COCH_3$	238.7	12,500 7	246.6	17,500 7	247	17,000 7	247.8	17,000 7	247.8	20,000 7
$-CMe = \overset{+}{O}H$ (in H_2SO_4)	295.5	28,000 7	311.3	30,000 7	312.8	30,000 7	315	32,000 7	315.5	28,000 7
$-NH_2$	234.4	8,000 7	235.5	10,000 7					235.4	12,000 7
$-O^-$ (in 0.1N NaOH)	234.5	11,000 7	235.9	9,500 7					235.7	13,000 7

to affect appreciably the spectrum. On determining of the spectra in acid media, an interesting development takes place. No longer are the spectra of methyl- and t-butyl-substituted compounds approximately equal, but there is now a marked change in the order of their inductive effects. A similar, even more pronounced effect, is reported for the maximal absorption of other carbonium ions.[7] This suggests that under those conditions the inductive effect has been increased considerably.[25]

To verify this, and also to investigate the effect of methyl substituents generally, the spectra of ortho- and para-methylbenzaldehydes and those of ortho- and para-methylpropiophenones have been determined in acid media (See Table VIII).

TABLE VIII

MAXIMA ($m\mu$) OF B-BANDS OF COMPOUNDS $Me.C_6H_4.CO.R$. IN ABSOLUTE ETHANOL AND SULPHURIC ACID.

	R = H (Benzaldehyde)				R = C_2H_5 (Propiophenone)			
Solvent	ortho-		para-		ortho-		para-	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
EtOH [12]	251	13,000	251	15,000	240	8,000	249	14,000
conc. H_2SO_4	296	17,000	310	23,000	296	19,000	310	23,000

Both pairs of compounds, in neutral solution, give spectra which can satisfactorily be accounted for by considering mesomeric and steric effects only. The changes observed in acid solution, however,[12,13,14] show that the transition probability, (for example the ortho compound) is very greatly increased compared with the expected value for an almost non-hindered (R = H) or slightly sterically hindered (R = C_2H_5) compound (see Table VIII). This suggests, that under these conditions,

the inductive effect also operates appreciably. Since the spectra in neutral solution follow quite a different pattern, it seems reasonable to ascribe the wavelength change due to the methyl group in neutral solution, predominantly to the mesomeric effect. This supposition is supported by (1) the spectra of ortho- and para-substituted methyl compounds which, in the absence of steric effects, are approximately equal in neutral solution and (2) the theoretical considerations[13] already referred to under that section. The data in Table VIII further indicate that the determinations in acid media are of less value in the study of mesomeric effects.

Since now there is some evidence for a predominant mesomeric effect of the methyl-froup, a tentative explanation, on a similar basis, may be made of the second-order changes observed on passing from methyl- to tert-butyl substituted compounds. It may be assumed that if one of the substituents in a para-disubstituted benzene compound has a negative or zero mesomeric effect, the benzene-ring is insufficiently activated to allow the additional positive mesomeric effect (due to the tert-butyl group) to operate. However, if the non-alkyl-substituent possesses a positive mesomeric effect (for example $-NH_2$ or $-O^-$) the additional mesomeric effect, due to the tert-butyl group, just becomes

detectable. This is evidenced from a very slight change in the correct order, namely -Me > -Bu^{t}. Hence, a mesomeric effect for alkyl groups in the order -Me > -Et > -Pr^{i} > -Bu^{t} cannot perhaps be ruled out completely. Unfortunately also, mesomeric and inductive effects have been shown to interact unless both are small. It would therefore be of little[22] value to attempt to obtain data for the mesomeric effect of alkyl groups by the method of simple subtraction.

Mesomeric effect variations among alkyl groups are thus very difficult to determine. Since light absorption data probably provide the most trustworthy physical evidence, there seems little hope of obtaining conclusive evidence from other physical properties, which observation receives support from the recent work of Schubert and Sweeney.[25]

EXPERIMENTAL

Instrument

The instrument used in this work was a Unicam SP500 Photoelectric Quartz Spectrophotometer. The spectrophotometer is used to measure the amount of radiant flux which is absorbed by a solution of a substance relative to that absorbed by the solvent alone. It consists of the following essential parts:

1. A source of radiant energy which is provided by a tungsten lamp for use from 1000 to 320 mμ and a hydrogen discharge tube for 320 - 200 mμ range. The hydrogen discharge bulb is operated from a controlled voltage supply and the tungsten bulb from a storage battery.
2. A monochromator, which employs a 30^{o} prism as a dispersing device. The light enters the prism through a narrow entrance slit and is dispersed into a spectrum which is focused at an exit slit, thus a portion of the energy is selected and allowed to pass into the material being studied.
3. Two absorption cells, one of which holds the solvent and the other the solution under investigation. The cells used in this work were 1 cm. silica cells.
4. A device for receiving and measuring the radiant flux. A photocell receives light from the absorption cells and the output is measured by balancing with a slide wire potentiometer.

Computation of Results

The Beer-Lambert Law states that the fraction of incident light absorbed is proportional to the number of absorbent molecules (n) in the light path.

$$\log_{10} \frac{I_o}{I} = kcl$$

I_o = intensity of incident light

I = intensity of transmitted light

c = concentration

l = cell length

$$\log_{10} \frac{I_o}{I} = E \text{ (absorbency)}$$

k = constant

If c is expressed in moles per litre and l in cm., k is represented by ε which is known as the molecular extinction coefficient and is then the absorbency of a sample 1 cm. thick and having a concentration of 1 mole per litre.

$E = E^{1\%}_{1cm} \times c$, where E is the "absorbency 1% 1cm." (c in % w./v.)

$E = E^{1}_{1} \times \frac{M.W.}{10}$ where M.W. is Molecular Weight.

Thus if 0.5 mg. sample is dissolved in 100 ml. solvent to give an absorbency reading E_{max} of 0.4 using a 1 cm. cell

$$E^{1}_{1} = \frac{0.4}{0.5 \times 10^{-3}}$$

$$\varepsilon = .8 \times 10^{3} \times \frac{M.W.}{10}$$

$$= \frac{8 \times 10 \times M.W.}{}$$

The wave length of light absorbed is determined by the energy of transition involved ($\Delta E = hc/\lambda$) and the intensity of absorption is related to the probability of the transition ε_{max} thus corresponds to the most probable transition.

Preparation and Purification of Materials

Any values which bear no reference were obtained by the author. In addition to these the values for p-fluoro-, p-chloro-, p-bromobenzaldehydes were checked and the experimental data for these are recorded below.

isopropylbenzene

Commercial sample was purified by vacuum distillation to constant refractive index ($\eta_D^{22.8}$ 1.4905). This was added to a known weight of ethanol in a covered volumetric flask to eliminate volatilization.

t-butylbenzene

Commercial sample was purified by vacuum distillation to constant refractive index ($\eta_D^{23.5}$ 1.4912) and was treated in same manner as preceding sample.

o-tolualdehyde

This was prepared according to a method by Sicé (J. Org. Chem. 19, 70 (1954)) o-tolyllithium (0.4 g atom) from o-bromotoluene was forced by nitrogen into an ice cold solution of dimethylformamide (0.2 mole) and yellow suspension stirred overnight and then poured onto ice. The solvent layer was washed with water, dilute hydrochloric acid, aqueous sodium bicarbonate and again with water. The solution was dried over sodium sulphate and residue vacuum

distilled to constant refractive index ($n_D^{22.5}$ 1.5480).

p-tolualdehyde

This was prepared by the Gatterman and Koch reaction as described by Coleman and Craig (Org. Syn. Coll. Vol. II, 583). It was vacuum distilled to constant refractive index (n_D^{22} 1.5460).

o-methylpropiophenone and p-methylpropiophenone

These were prepared by W.A. Mueller of this laboratory. The refractive indices were respectively, n_D^{22} 1.5243 and n_D^{23} 1.5627.

p-fluorobenzaldehyde and p-bromobenzaldehyde

These were prepared by bromination of the side chain of corresponding toluenes according to the method by Coleman and Honeygold (Org. Syn. Coll. Vol. II, 89). The former was purified by vacuum distillation to a constant refractive index ($n_D^{22.2}$ 1.5200) and the latter by vacuum sublimation (m.p. 56°).

p-chlorobenzaldehyde

Commercial sample was crystallized in aqueous ethanol (m.p. 47°).

SPECTRAL DATA

COMPOUND	SOLVENT	CONC. (mg./100 ml.)	λ_{max}	E_{max}	$\varepsilon \times 10^3$	$\varepsilon \times 10^3_{ave}$
isopropylbenzene	EtOH(Abs)	0.62	207	0.459	8.9	
"	"	0.66	207	0.481	8.7	8.7
"	"	0.64	207	0.461	8.6	
t-butylbenzene	"	0.77	206.5	0.520	9.0	
"		0.58	206.5	0.404	9.0	8.9
"	"	0.80	206.5	0.520	8.7	
o-methylpropiophenone	H_2SO_4(96%)	0.38	296	0.480	19.0	19
"	"	0.40	296	0.528	18.6	
p-methylpropiophenone	"	0.36	310	0.578	24.2	23
"	"	0.34	310	0.490	22.0	
o-tolualdehyde	"	0.30	296	0.421	17.0	17
"	"	0.39	296	0.570	17.7	
p-tolualdehyde	"	0.32	309	0.618	23.0	23
"	"	0.32	309	0.620	23.0	
p-fluorobenzaldehyde	EtOH(Abs)	0.49	245	0.472	11.9	12
"	"	0.41	245	0.402	12.0	
p-chlorobenzaldehyde	"	0.49	254	0.537	15.4	15
	"	0.48	254	0.525	15.3	
p-bromobenzaldehyde	"	0.49	257	0.409	15.5	16
	"	0.52	257	0.449	16.4	

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